1. Introduction

Microwave special effects are well known to accelerate chemical reactions, shorten the completion time of chemical synthesis, and increase chemoselectivity in both homogeneous and heterogeneous chemical reaction systems. However, these so-called microwave special effects may only be artifacts of inappropriate experimental methods.

Microwave special effects have been widely reported for hydrodesulfurization of thiophene (exothermic) and decomposition of hydrogen sulfide (endothermic) on MoS$_2$/Al$_2$O$_3$, enhanced reactions of steam-carbon and water-gas shift reactions, and enhanced reduction of copper oxide under microwave magnetic-field irradiation by coupling of the H-field with the Fermi level electrons of CuO, resulting in cleavage of the Cu-O bond. Two aspects of microwave special effects were recently discovered supported by carefully designed experiments. Both phenomena are especially observed in heterogeneous systems containing solids, specifically at solid-solid and liquid-solid interfaces.

The present review describes nonequilibrium local heating as an origin of microwave special effects.

2. Nonequilibrium Local Heating as an Origin of Microwave Special Effects

2.1. What is Nonequilibrium Local Heating?

Microwaves interact with molecules and are converted into heat through various mechanisms, such as dielectric heating, joule heating, and magnetic heating, as expressed as in Eq. (1).

$$ p = \frac{1}{2} \sigma [E]^2 + \rho \epsilon_0 \epsilon_r [E]^2 + p f \mu_0 \mu_r [H]^2 $$

Each term of Eq. (1) contains the parameters of resistivity, dielectric loss factor, and magnetic loss factor, which depend on the molecular structures. These specific mechanisms lead to specific and unusual heating.
modes only achieved by microwave irradiation, *i.e.*, rapid heating, internal heating, and molecule-selective heating. Nonequilibrium local heating especially occurs at solid-solid, liquid-solid, and gas-solid interfaces (Fig. 1). Nonequilibrium local heating was first observed at the surface of Co particles dispersed in dimethyl sulfoxide (DMSO) as described in the next section.

### 2. 2. In-situ Observation of Nonequilibrium Local Heating: Cobalt Particles Dispersed in Liquid Medium

Higher temperature of DMSO molecules in close proximity to Co metal particles were observed *in-situ* under microwave irradiation. The key method for measuring the local temperature of only these specific DMSO molecules was a Raman spectrometer especially designed for *in-situ* detection of signals from solutions under microwave irradiation. Raman spectrometry can determine the temperature of the targeted substance because the ratio of the Stokes and anti-Stokes lines is a function of the temperature. The Raman spectrometer used was equipped with a probe made of Teflon, since Teflon has little interaction with microwaves. The Raman probe was inserted into the DMSO solution containing Co particles under stirring and to continuously record the Raman spectra under microwave irradiation. The average temperature of the dispersion solution was monitored with a fiber-optic thermometer.

**Figure 2** exhibits the temperature rise of the bulk solution determined by the fiber-optic thermometer (black line) and the temperatures estimated by the Raman spectroscopy during microwave irradiation. High temperature spikes were randomly observed by Raman spectroscopy during microwave irradiation, demonstrating the occurrence of localized high temperatures in the limited region observed by the Raman probe. The detection region of the Raman probe is 10-20 μm, so this localized high temperature occurred in DMSO molecules heated more than molecules in the bulk solution. Such localized heating was explained as selective heating of DMSO molecules in close proximity to the surface of Co particles, which are selectively heated by microwave irradiation. This phenomenon was named nonequilibrium local heating.

### 2. 3. Nonequilibrium Local Heating Observed in Solid Catalysis: Zeolite Including Carbon Core

Here, we introduce an example of using a core-shell structure of zeolite to design a solid catalyst that fully exploits the effects of microwave nonequilibrium local heating. The core part and shell are formed in one zeolite particle by multistage synthesis, and can impart different characteristics to each other. Based on the zeolite characteristics in a form suitable for microwave heating, a reaction field was exclusively formed under microwave irradiation in a solid catalyst dispersion system. One of the main features of microwaves is the selective heating of substances that interact well with microwaves. The zeolite used in this experiment was little heated by microwaves, whereas carbon is well known as a substance heated by microwave irradiation. By filling the pores of the core zeolite with carbon, an exothermic field which generates more heat under microwave irradiation was formed. This core zeolite was coated with shell zeolite, resulting in core-shell zeolite. The shell zeolite functioned as a reaction field by ion-exchanging cations in the shell zeolite with protons to form an acid catalyst.

This core-shell type zeolite was used as a catalyst for the dehydration reaction of 1-phenylethanol under microwave irradiation in *n*-heptane solvent. The same reaction was carried out using a normal zeolite without a core part as the control experiment. In this reaction, two products were generated, olefin by intramolecular dehydration and ether by intermolecular dehydration (Fig. 3(a)). Using the core-shell zeolite, the amounts of both reaction products under the boiling point of heptane were higher using microwave heating than conventional heating (Fig. 3(b)). On the other hand, using the normal zeolite, the yields were similar with microwave heating and conventional heating (Fig. 3(c)). Therefore, the temperature of the reaction field was higher than the boiling point of heptane in the core-shell zeolite under microwave heating. In other words, the core zeolite part filled with carbon was selectively heated.
heated by the microwaves unlike the solvent, so that the heat reached the shell zeolite part acting as the reaction field and promoted the reaction.

The actual temperature in the reaction field was estimated using Arrhenius plots of the reactions under conventional heating. The reaction was carried out at various temperatures by mixing heptane and octane to control the boiling point of the solvent. The activation energies obtained were 83 kJ/mol and 88 kJ/mol for formation of the olefin and ether, respectively. From the Arrhenius plot, the enhancements of reactions under microwave heating were estimated to correspond to temperature differ ences of +6 K in the case of the olefin, and +11 K in the case of the ether compared to conventional heating. Therefore, using the core-shell zeolite filled with carbon in the core, local regions were formed in the shell are heated to 6-11 K higher than the surrounding solvent.

Such design of a catalyst structure will allow catalytic reaction under microwave irradiation with high efficiency.

2.4. Nonequilibrium Local Heating Observed for Contacted Layers

One of the most important advantages of microwave heating over conventional heating is the selective heating due to the interaction between the applied electromagnetic field and electrons, electric dipoles and magnetic dipoles in molecules. Microwave irradiation heats the bulk material directly, and does not require any heat transfer medium surrounding the target material. On the other hand, a disadvantage of microwave heating is that materials which do not interact with an applied electromagnetic field are impossible to heat. This specific feature of microwave heating critically limits the areas of application, since the fundamental material characteristics, electric conductance and imaginary part of the permittivity and permeability, cannot be engineered independently. Another option to heat the target materials is to tune the frequency of the incident electromagnetic waves, since the dielectric properties of materials depend on this frequency. However, the use of microwaves in industry is severely restricted in certain bands, typically 2.45 GHz and other several bands by national laws controlling radio waves mainly for telecommunications. Consequently, most commercially available microwaves adopt the frequency of 2.45 GHz which may not allow heating of all types of materials, generally due to the absence of the imaginary part of permittivity and permeability of the target material in the corresponding frequency range, despite the strong advantage of this frequency for the heating of water, carbon, silicon carbide, etc.

Recently, a new heating phenomenon was identified in which materials with weak microwave absorption occasionally show enhanced microwave heating if structured in a layered configuration (Fig. 4). This finding provides significant potential not only to extend the applications of microwave heating, but also to engineer the targets for nonequilibrium local heating at the interface of materials for novel applications in nanomaterial processing, such as solid-state catalysts, nanocomposites, and layered film device fabrications. Further investigation is still required to elucidate the mechanism of the heating phenomena, but it may be based on Maxwell-Wagner type heating attributed to the perturbation of interfacial electric dipoles by incident oscillating electric fields.

This interfacial microwave heating phenomenon was first applied to the annealing process of TiO2 nanoporous films on transparent conductive glass (F:SnO2) for a photovoltaic device, dye-sensitized solar cells (DSSCs). The products consistently exhibited better device characteristics in addition to one order of magnitude shorter annealing process time. This enhancement of cell properties was attributed to improvement of the minority carrier transport in the layered film electrode based on the diffusion length analysis of electrons in the TiO2/F:SnO2 electrode. Therefore, improvement of the diffusion length resulting from better interfacial contact properties and film quality was proposed to occur, since the TiO2/F:SnO2 interface is selectively heated under microwave irradiation. Various studies of microwave applications to improve the film...
Another application was proposed to improve the charge transfer at the interface of nanoparticles adsorbed on oxide semiconductor materials. Photocatalytic materials based on semiconductors typically consist of co-catalyst nanomaterials deposited on the mother semiconductor, which generates the minority carriers of electrons and holes. Such photogenerated carriers are ideally gathered at the co-catalysts, where the chemical reaction occurs under photo irradiation. Therefore, reducing the energy loss in the carriers at the interfaces before transmission to the co-catalyst surface is one of the most important issues to improve the characteristics of photocatalysts. Interfacial microwave heating was applied to manufacture of CoO$_x$/Fe$_2$O$_3$ for the photocatalysis of water to create oxygen for water splitting reactions. Microwave irradiation was applied to the materials during the construction of the CoO$_x$ co-catalysts by photochemical deposition on Fe$_2$O$_3$ semiconductor. The resultant CoO$_x$/Fe$_2$O$_3$ photocatalyst exhibited improved photoelectrochemical properties compared with the reference sample made using conventional oil bath heating. Photoelectrochemical analysis based on impedance spectroscopy attributed this improvement to interfacial carrier transfer due to the lower resistance and capacitance at the interface. This result is important not only because interfacial microwave heating improved the interfacial carrier transfer, but also for the application to the interface of nanosized materials.

Therefore, application of interfacial microwave heating to construction of nanosize materials opens new directions for research. A series of novel metal nanoparticles, such as Pt, supported on oxide mother materials can be heated under microwave irradiation, and similar effects of interfacial heating were observed. Consequently, interfacial heating of metal nanoparticles/oxide could be applied for metal nanoparticle-based solid-state catalysis. Research to elucidate the advantages of microwave interfacial heating applied to solid-state catalysis is continuing.

2. 5. Nonequilibrium Local Heating Observed for Solid-solid Reactions: Microwave-driven Smelting of Mg

Magnesium (Mg) alloys have low density and lightweight characteristics so are desirable replacements for Al alloys in the automotive industry as well as the aviation industry, because the subsequent reduction in the weight of components results in improvement in fuel economy. Mg also has the highest internal energy density for electricity, so batteries using Mg as a negative electrode have higher power storage capacity than Li ion batteries.

Currently, smelting of magnesium metal is mainly performed using the Pidgeon method (thermal reduction method) in which dolomite ore and ferrosilicon are heated to high temperatures (1200-1400 °C) and the evaporated magnesium is condensed to obtain magnesium metal using a large amount of coal as the heat source. About 80% of magnesium metal is produced in China. A large amount of coal is consumed for magnesium smelting, resulting in generation of fine particulate matter (PM 2.5) and release of carbon dioxide into the atmosphere, which both cause major problems.

$$2\text{MgO(s)} + 2\text{CaO(s)} + (\text{Fe})\text{Si(s)}$$
$$\rightarrow 2\text{Mg(g)} + \text{Ca}_2\text{SiO}_4(s) + \text{Fe(s)}$$

s: Solid, g: Gas
Dolomite mineral: MgO, CaO
Ferrosilicon: FeSi
Heat source: Coal

A novel Pidgeon process powered by microwaves, called the microwave Pidgeon process, has been developed to produce Mg metal with less energy consumption and no direct CO$_2$ emission. Normally, dolomite is a poor absorber of microwave energy and so is not heated. However, the microwave energy could be absorbed by briquettes by using ferrosilicon as the reducing agent, manufacturing the raw material pellets obtained by mixing dolomite and ferrosilicon in a shape...
with a resonance structure of 2.45 GHz. Figure 5(a) shows the schematic of five briquettes which correspond to one wavelength of 66 mm, and the diagonal and cross-sectional views of the briquette. Internal heating and contact point heating characteristic of microwave heating were observed, and the average reaction temperature for smelting was lowered from the conventional temperature to 1000°C.

Using a small-scale experimental reactor, 1 g of magnesium metal was smelted successfully. Figure 5(b) shows the X-ray diffraction pattern of the Mg condensed on the quartz tube. All peaks were identified as Mg crystal face numbers. The inset shows a photograph of the metal sample with a diameter of 18 mm, maximum length of 20 mm, and thickness of 1 mm.

To accurately estimate the energy consumption, a demonstration furnace about 5 times larger than the experimental furnace was manufactured and experiments were conducted, resulting in the successful smelting of about 7 g of magnesium metal. Energy consumption was 31.4% of the conventional method.

3. Acceleration of Electron Transfer

Acceleration of electron transfer reactions is crucial for increasing the efficiency of solar energy conversion systems. Conventionally, modification of the components in solar energy conversion systems including photo-antennas, electron mediators, and solvents is the only way to control the rate of electron transfer reactions. Recently, acceleration of electron transfer reactions at the surface of semiconductors was achieved by remote input of an external microwave field without changing the geometries or materials of components in the systems. Both reduction of organic molecules and oxidation of water at the surface of semiconductor particles are accelerated by 2.45 GHz microwave irradiation. Therefore, microwave irradiation is expected to enhance artificial photosynthesis systems by using water as an electron source.

3.1 Microwave-accelerated Electron Transfer Observed for CdS Nanoparticles

Enhanced photocatalytic reduction of bipyridinium by CdS nanoparticles under microwave irradiation was investigated using N,N'-bis(3-sulfonatopropyl)-4,4'-bipyridinium (PVS) as an electron acceptor, and CdS nanoparticles anchored on SiO2 particles as a photocatalyst. The concentration of anion radicals of PVS can be determined using UV-Vis spectroscopy. Figure 6(a) shows the time variation plots of the anion radical concentrations under microwave and conventional heating. Both systems were maintained at 52°C. The generation rate of anion radicals was two times faster under microwave heating than under conventional heating, demonstrating enhancement of the photocatalytic activity of CdS nanoparticles.

The rate of electron transfer from photoexcited CdS nanoparticles to PVS was investigated by measuring photoemission decays of CdS nanoparticles on the sub-nanosecond order under microwave and conventional heating. By using time-resolved spectroscopy, the adsorption and desorption processes could be excluded, and only the electron transfer process was studied, because the time constants of the adsorption and desorption of the electron acceptor molecules are extremely slow compared with those of electron transfer. Photoemission at 520 nm (excitation of 365 nm) was measured, which is attributed to the photoemission process from a surface defect level of CdS nanoparticles, for the analysis of time-resolved emission decays. CdS nanoparticles adsorbed on a mesoporous SiO2 substrate were immersed into an aqueous solution of PVS.
Temperature measurements were performed using a fiber-optic thermometer (Opsens, Picosens) installed in the liquid phase and close to the CdS nanoparticles on SiO2 substrate. Microwave input power was 1.0 W, and the system was maintained at 52 °C by balance of absorption of microwave energy and heat dissipation. The control experiment was also maintained at 52 °C under conventional heating. The time-resolved emission decay profiles of CdS nanoparticles immersed in pure water or aqueous PVS solution are shown in Fig. 6(b). No change was seen in water under microwave irradiation, suggesting that the luminescence and non-luminescence processes in CdS nanoparticles were unaffected by microwave irradiation. In contrast, the emission lifetime of CdS nanoparticles immersed in PVS solution was clearly shortened under microwave irradiation. These findings demonstrated that microwave irradiation can accelerate the photoinduced electron transfer reaction from CdS nanoparticles to PVS in the liquid phase.

To exclude the effect of local heating of CdS nanoparticles, the time-resolved emission decay profiles of CdS nanoparticles immersed in the PVS solution were measured under conventional heating at 42, 52, and 62 °C (Fig. 6(c)). The decay curve remained the same at all temperatures. Therefore, we suggest that the change in the emission lifetime under microwave irradiation was not caused by nonequilibrium local heating. These findings demonstrated that microwave irradiation does not cause acceleration of local heating in CdS nanoparticles, but by microwave non-thermal effects shown by the acceleration of excited electron transfer from CdS nanoparticles to PVS.

The rate constant of electron transfer can be estimated from the decay curves. The obtained electron transfer rates from CdS nanoparticles to PVS under microwave irradiation and conventional heating were 2.6 × 10^{11} M^{-1} s^{-1} and 1.0 × 10^{11} M^{-1} s^{-1}, respectively. These values clearly demonstrate acceleration of the transfer of excited electrons. To understand the mechanism of acceleration of electron transfer, we employed the Marcus theory of non-adiabatic electron transfer reactions which suggests that electronic coupling between CdS nanoparticles and PVS was enhanced under microwave irradiation. Therefore, we proposed that acceleration of electron transfer is caused by the collective vibration of electrons in CdS induced by microwave irradiation.

3.2. Microwave-accelerated Electron Transfer Observed for Water Oxidation on a Hematite Electrode

Acceleration of water oxidation on a hematite (α-Fe2O3) electrode was demonstrated under microwave irradiation. Since water is used as an electron source in artificial photosynthesis systems, water oxidation is extremely important for solar energy conversion. However, oxidation of water is slow at the surface of semiconductors, and generally causes a problem for artificial photosynthesis systems. Therefore, acceleration of water oxidation by microwave irradiation will open a new strategy for the development of efficient solar energy conversion systems.

An FTO electrode coated by α-Fe2O3 nanoparticles (α-Fe2O3/FTO) was fabricated by an electrodeposition method. The α-Fe2O3 nanoparticles formed aggregations with sizes of 10-100 nm. The thickness of the α-Fe2O3 layer was determined as ca. 700 nm using a DektakXT Stylus Profilometer. Electrochemical measurements were performed using a three-electrode system in two cells connected by a salt bridge as shown in Fig. 7(a). The main cell made of quartz transparent to microwaves (Fig. 7(b)) was placed into the 2.45 GHz waveguide-type single mode microwave cavity. The tip section of the main cell targeted by microwave irradiation was 5-mm thick and 50-mm long. A fiber-optic thermometer was introduced close to the electrode. Another cell connected electrochemically with the main cell through a salt bridge was positioned outside the microwave waveguide. Microwaves were irradiated only onto the main cell containing the working electrode.
The onset of the anodic current attributed to water oxidation was observed at about 1.5 V versus RHE for the \( \alpha \)-Fe\(_2\)O\(_3\)/FTO electrode immersed in 0.1 M NaOH\(_a\)q under ambient conditions. Subsequently, the main cell was positioned at the antinode of the oscillating electric field where the electric field is maximum in the cavity. Then, the potential of the \( \alpha \)-Fe\(_2\)O\(_3\)/FTO electrode was set at 1.966 V versus RHE and the electrode was intermittently irradiated with microwaves for periods of approximately 1 s. Figure 7(c) shows the measurements of the anodic current of the electrode. Rectangular waves were observed under pulsed microwave irradiation. The current density increased from 0.17 to \( \sim \)0.22 mA cm\(^{-1} \) simultaneously with microwave irradiation. Moreover, the current density was maintained at \( \sim \)0.22 mA cm\(^{-1} \) during microwave irradiation, but fell to 0.17 mA cm\(^{-1} \) without microwave irradiation. The steady increment in the anodic current density was attributed to enhancement of water oxidation on the surface of the \( \alpha \)-Fe\(_2\)O\(_3\)/FTO electrode by the oscillating electric field induced by microwave irradiation.

The specific morphology of the \( \alpha \)-Fe\(_2\)O\(_3\) on the FTO substrate is crucial for microwave enhancement of the oxidation, as the mechanism of microwave enhancement is related to the interaction between the \( \alpha \)-Fe\(_2\)O\(_3\) nanoparticles and microwaves. In contrast, water reduction at the surface of a Pt disc electrode was accelerated due to the thermal effects of microwave irradiation\(^{21} \). Microwaves can penetrate into solid \( \alpha \)-Fe\(_2\)O\(_3\), whereas the solid Pt reflects microwaves because of its high carrier density, resulting in localized high temperature proximal to the electrode which promotes the water reduction reaction. These observations indicate that the interaction between the solid substrate and the microwaves are key to the acceleration of electron transfer reactions.

4. Future Aspects

This article describes various studies of the special phenomena observed under microwave irradiation, which must be understood as the origins of microwave special effects. We are now concentrating on the experimental and theoretical investigation of non-equilibrium local heating and electron transfer acceleration occurring in the well-ordered structures of solids under microwave irradiation using spectroscopic methods to understand the mechanisms. We believe that control of catalytic reactions and solid reactions by microwave irradiation will be possible by systematically understanding such mechanisms.

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References

要 旨
マイクロ波特殊効果に関する科学的洞察 - 非平衡局所加熱と電子移動加速 -

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マイクロ波照射下での化学反応においてのみ観察される「マイクロ波特殊効果」の起源として、マイクロ波照射下で誘導される固体内界面で発生する新たな反応を提案する。著者らは、第1の現象としてマイクロ波照射下での固体と接触面間の接触点で観察される発熱現象を示し、これを「非平衡局所加熱」と呼んでいる。

マイクロ波照射下での in-situ ラマン光測定によって、DMSO 中に分散したコバルト金属粒子に非平衡局所加熱が生じることを実証した。また、ゼオライト粒子のコーラに炭素を配置することによって非平衡局所加熱を生じ、ゼオライトの細孔内でのアルコール脱水反応の促進が可能であることを示した。第2の現象は、マイクロ波照射下での固体表面において生じる「電子移動の加速効果」であり、硫化カドミウム誘導体の光還元応答やヘマタイト電極の表面での水の酸化反応において実証した。